AN INVESTIGATION OF THE CHEMISTRY OF THE PORE STRUCTURE OF COAL IN THE PRESENCE OF A SWELLING SOLVENT USING A NOVEL EPR TECHNIQUE

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KEYWORD: Porosity, coal swelling, EPR, nitroxyl spin probe

ABSTRACT

To study the hydrogen bonding ability of functional groups in pores of Argonne Premium Coal Samples (APCS) exposed during swelling, small nitroxide spin probes with reactive R groups differing in polarity were diffused into APCS coals during swelling and the concentration of the trapped probes measured by an EPR method. As the hydrogen bonding ability of R increases, the degree of probe retention increases; however, probe retention decreases with rank. Polar solvents like pyridine interact specifically with polar functional groups on the micropore wall and prevent binding with polar guest molecules.

INTRODUCTION

The pore structure of coal plays an important role in the behavior of coal during mining, benefaction, and utilization. The pore structure of coal has three components, macropores (>300 Å diameter), mesopores (300 - 12 Å diameter) and micropores (< 12 Å diameter). The micropores make up as much as 88% of the total pore volume of low rank coals and up to 12% of the total pore volume of anthracites (1). Since most of the surface area of coals is located in the micropores (2), rates of reaction are limited by rates of diffusion through the micropore structure.

The micropore structure has been studied by several methods. Helium adsorption is the oldest method(3,4). More recently, small angle x-ray scattering (SAXS) (5,6) and small angle neutron scattering (SANS) (7,8), have been used to examine the micropore structure of coal. The micropore system undergoes changes in the presence of swelling solvents. Gethner showed that weakly swelling solvents such as cyclohexane do not change the micropore structure significantly from the dry state (9). Gethner (8), Winans and Thiyagarajan (7) showed that in the presence of benzene, micropores were spherical in shape. In the presence of pyridine, pores become elongated and cylindrical.

B. G. Silbernagel et. al. (10) first expanded EPR to examine guest molecules incorporated into coal. Silbernagel (10) wanted to study guest molecule inclusion into coals. He used 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPOL (Figure 1), as a probe. TEMPOL is a stable free radical and gives a highly articulated EPR spectrum. In the presence of coal, the center peak is overlapped by the carbon radical peak. Over several hours, the TEMPOL signal broadens and diminishes. However, the total spin density remains constant during this time, implying that TEMPOL is not being destroyed. The broadening occurs when the rate of motion of TEMPOL molecules drops below the value need for motional narrowing (10^8 sec^{-1}). The restriction of motion implies that, since the TEMPOL is not being destroyed, it must be included in the coal matrix (10).

To study the dynamics of the inclusion process, Silbernagel et al. (10), measured the derivative height of the TEMPOL spectrum as a function of time for Illinois No. 6 hvb coal swelled with benzene. A rapid reduction of the derivative intensity was observed after the first few minutes, indicating that adsorption had taken place. After the first few minutes, the reduction of derivative intensity became slower. A plot of the product of derivative intensity and $t^{1/2}$ versus time indicated that TEMPOL was indeed diffusing into the coal. With these experiments, Silbernagel et al. had developed a unique method for investigating the microporosity of coal (10).

Kispert and coworkers expanded on this technique to study the effect of low temperature swelling on the micropore system of coal. Wu and Kispert (11) showed that a wide variety of spin probes could

be incorporated into coal to study the micropore structure of coal. Cooray (12) studied the mechanism of probe interaction with coal by measuring $2A_{zz}$ as a function of temperature. Cooray concluded that at temperature above 220 K the spin probes exhibited no significant interaction with coal (12). Goslar and Kispert (13) conducted electron double resonance spectroscopy (ENDOR) on coals doped with nitroxyls and confirmed the absence of significant coal-spin probe interaction, at least through the N-O bond.

The effect of low temperature swelling conditions on pore size and shape has been extensively studied by Spears et al. (14,15). Coals contain spherical pores when swelled at low temperature and with a mild swelling solvent. Upon swelling with hydrogen bonding solvents such as nitrobenzene or pyridine, pores become elongated and cylindrical. The degree of elongation is dependent on both the polarity of the swelling solvent and the swelling temperature. To determine the number of spherical probes present TEMPOL was used as a spin probe. TEMPOL, although spherically shaped, has an -OH group which could potentially interact with the coal. Gethner has recently shown that pore walls in coal are covered with oxygen functionalities. (16) Although it was known that nitroxyls did not interact significantly at 300 K with coal through the N-O bond, it was thought that the polar R group of TEMPOL might.

To understand the chemistry of the micropore walls, a series of similarly sized nitroxyls were incorporated into the micropore structure of Argonne Premium Coal Sample (APCS) coals. The effects of rank, swelling solvent polarity, swelling temperature, and drying of the coal were investigated.

EXPERIMENTAL

The experimental procedure has been described elsewhere in detail (11-15). Spin probes were imbibed into the pore structure of coal in the presence of a swelling solvent. The solvent was removed, causing the pore structure to collapse about the incorporated nitroxyls. The coal was then washed with cyclohexane. If the spin probe was unable to penetrate a pore because it had not swelled open sufficiently, it was removed in the cyclohexane wash. If the probe molecule was trapped in a pore much larger in size, it was also removed in the cyclohexane wash. Thus, after the cyclohexane wash, all probes retained were trapped in pores similar in size and shape to the nitroxyl molecule.

The general structural shape of the spin probes used in this study are shown in Figure 1 where R represents the substitutent for each spin probe. The specific spin probes are numbered in the same manner as defined previously (12). Spin probe VIII, 2,2,6,6-tetramethylpiperidine-1-oxyl, is the basic structural unit for all nitroxyl spin probes studied. Spin probes VIII, I, VI, and VII are similar in size (molecular volume approximately 140 $Å^3$) and are spherically shaped. Spin probe X is larger (molecular volume 310 $Å^3$) and cylindrically shaped. All eight APCS coals were studied (Table 1). Coals were swelled in either toluene or pyridine at 333 K for 18 hours. Spin probe concentration was determined by EPR and normalized to 1 g of coal.

DISCUSSION

The number of spherically shaped micropores was determined by imbibing spin probe VIII into coal. Spin probe VIII should exhibit no significant interaction with coal. The results of swelling coal at 333 K with solutions of spin probe VIII are shown in Figure 2 as a function of rank and swelling solvent. Carbon content was used as convenient rank indicator throughout this study. For coals swelled in toluene, the number of small, spherically shaped pores is small such as for Beulah-Zap lignite and Wyodak subbituminous coals (74 and 76% carbon, dmmf, respectively), and quickly fall to zero as rank increases. In pyridine at 333 K, none of the APCS coals retained spin probe VIII. This indicated that all of the small, spherically shaped micropores had vanished.

Comparing the results with spin probe X, a spin probe larger than spin probe VIII and cylindrical in shape, shows that the micropores are enlarged and elongated. Figure 3 shows the change in spin probe X and VIII concentration with carbon content for coals swelled in either toluene at 333 K. The coals retained larger concentrations of spin probe X than spin probe VIII. This showed that the micropores were indeed becoming elongated.

Pore elongation in swelled coals meant that coals should not retain significant amounts of small, spherically shaped pores. However, previous data showed that coals swelled in toluene retained significant amounts of spin probe I and 333 K, especially compared to spin probe VIII. The main

difference between spin probe VIII and spin probe I was the polar R group. Thus the retention in coal was due to association of the -OH group with the pore walls.

Micropore walls, especially in swollen coals, are covered with polar functionalities. Gethner showed that micropore walls in low rank coals were linked with carboxylic acid groups (16). Coals contain significant amounts of hydrogen bonding. Hydrogen bonding in coal has been attributed to oxygen-containing functional groups. The swelling of coal in polar solvents has been ascribed to the disruption of these bonds by solvent molecule interaction. As polar functionalities are exposed by the swelling solvent, spin probes with polar R groups should be retained. The degree of retention should be directly related to the hydrogen-bonding ability of the R group. As the hydrogen-bonding ability of the R group increased, the strength of the spin probe-coal interaction should increase.

To test this hypothesis, APCS coals were imbibed with 4 spin probes differing in the polarity of the R group in toluene at 333 K. The R groups were -H, -OH, $-CO_2H$, and $-NH_4$ (spin probes VIII, I, VI, and VII respectively). The results are shown in Figure 4. As the relative R group polarity increased, the degree of retention increased, especially for low rank coals. Although the micropore system was enlarged by toluene swelling at 333 K, polar spin probes were still retained. This indicated that spin probes with polar R groups were retained in macropores larger than the size of probe molecule itself. Retention was apparently due to interaction of the polar R group with the coal surface. This mechanism of retention was considerably different from the simple physical entrapment for other spin probes studied (11-15).

The polarity of the functional groups in the micropore walls is apparently low. Highly polar functionalities should show little specificity of retention between the spin probes studied. A knowledge of the dissociation constants or the electron donor numbers of the spin probes should give more specific details as to the polarity of coal function groups.

Low rank coals contain larger quantities of oxygen functionalities and so should retain more of polar spin probes. The degree of retention decreased with rank, and the influence of R group polarity decreased with rank, but even at the highest ranked APCS coals, the effect of R group polarity was still significant. These results showed that polar functionalities were still present even at high rank coals. These functionalities are likely responsible for the hydrogen bonding which earlier spin probe studies had indicated that existed in coal of all ranks (15).

If hydrogen bonding was indeed a factor in the coal tertiary structure, then swelling coal in pyridine at 333 K would disrupt the hydrogen bonding network considerably. Previously results showed that swelling coal in pyridine at 333 K caused considerable opening of the micropore structure (15). This could only be the result of disruption of the hydrogen bonding network. Such disruption, followed by solvent removal, could lead to the exposure of polar functionalities within the coal, and result in greater retention of polar spin probes.

To test this hypothesis, APCS coals were imbibed with 4 spin probes differing in the polarity of the R group in   pyridine   . The R groups were -H, -OH, $-CO_2H$, and $-NH_2$ (spin probes VIII, I, VI, and VII respectively). The results are shown in Figure 5. As for coals swelled in toluene, an increase in the relative R group polarity resulted in increased retention although the difference between spin probe VI and spin probe VII is negligible. However, a comparison of Figure 4 with Figure 5 shows that, for a given spin probe, coals swelled in pyridine retained fewer spin probes than coals swelled in toluene, contrary to expectations.

Green showed that molecules capable of hydrogen bonding interact with specific sites in coal. (17) Pyridine interacts strongly with coal, and is not entirely removed even under the most severe vacuum drying. It is possible that unremoved solvent molecules tied up existing hydrogen bonding sites, reducing the number of sites available for spin probe-coal interactions. If many of the reactive sites in coal are tied up, then the polar spin probes would be trapped in enlarged micropores with fewer sites available for specific interaction. This would result in removal during the cyclohexane wash. To examine the swelling characteristics of the APCS coals after drying, APCS coals are now being subjected to vacuum drying at either room temperature or at 100°C. Results of these studies will be presented.

CONCLUSION

In conclusion, micropore enlargement occurs as the degree of swelling increases. The micropore structure is held together by hydrogen bonding, which can be disrupted by swelling with polar solvents. The micropore walls contain polar functional groups. The number of these functional groups decreases with rank. Polar solvents like pyridine interact specifically with these sites and prevent them from bonding with polar guest molecules. Thus, using a strongly polar solvent to swell coal in conversion processes might actually defeat the purpose by tying up reactive sites.

REFERENCES

1. Gan, H.; Nandi, S. P.; Walker, P. L., Jr. *Fuel* **1972**, *51*, 272.

2. Mahajan, O. P.; Walker, P. L., Jr.; in *Analytical Methods for Coal and Coal Products*, C. Karr, ed., Academic, New York, **1978**, 162.

3. Nelson, J. R., Ph. D. Dissertation, Pennsylvania State University, State College, **1979**.

4. Fuji, S.; Tsuboi, H. *Fuel* **1967**, *46*, 361.

5. Spitzer, Z.; Ulicky, L. *Fuel* **1976**, *50*, 21.

6. Lin, J. S.; Hendricks, R. W.; Harris, L. A.; Yust, C. S. *J. Appl. Crystallogr.*, **1978**, *11*, 621.

7. Winans, R. E.; Thiyagarajan, P. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **1987**, *32*, 227.

8. Gethner, J. S. *J. Appl. Phys.* **1986**, *59*, 1068.

9. Gethner, J. S. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **1987**, *32*, 239.

10. Silbernagel, B. G.; Ebert, L. B.; Schlosberg, R. H.; Long, R. B. *Adv. Chem. Ser.* **1979**, *192*, 23.

11. Wuu, S. K.; Kispert, L. D. *Fuel* **1985**, *64*, 1681.

12. Cooray, L. S.; Kispert, L. D.; Wuu, S. K. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, **1988**, *33*, 32; Cooray, M. L. S., M.Sc. Thesis, University of Alabama, Tuscaloosa, 1988.

13. Goslar, J.; Kispert, L. D. *Fuel*, **1990**, *69*, 564.

14. Spears, R.; Goslar, J.; Kispert, L. D. in *Techniques in Magnetic Resonance for Carbonaceous Solids*, Botto, R., and Sanada, Y., eds., ACS Symposium Series No. 229, In Press.

15. Spears, R.; Kispert, L. D.; Piekara-Sady, L. *ACS Div. Fuel Chem. Prepr.* **1991**, *36*, 29.

16. Gethner, J. S. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **1987**, *32*, 239.

17. Green, T. K.; West, T. A. *Fuel* **1986**, *65*, 298.

Table 1. Major element composition of Argonne Premium Coal Samples, dmmf basis.

Coal	% C	% H	% N	% S	% O
Upper Freeport	88.08	4.84	1.60	0.76	4.72
Wyodak-Anderson	76.04	5.42	1.13	0.48	16.90
Illinois No. 6	80.73	5.20	1.43	2.47	10.11
Pittsburgh No. 8	84.95	5.43	1.68	0.91	6.90
Pocahontas	91.81	4.48	1.34	0.51	1.66
Blind Canyon	81.32	6.81	1.59	0.37	10.88
Lewis-Stockton	85.47	5.44	1.61	0.67	6.68
Beulah-Zap	74.05	4.90	1.17	0.71	19.13

POLAR SPIN PROBES   CYLINDRICAL SPIN PROBE
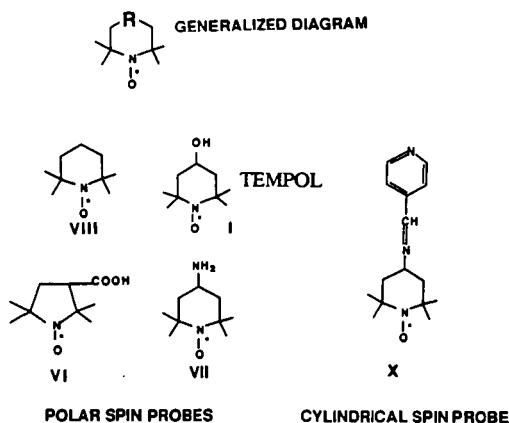
Figure 1.   Nitroxyls used as spin probes in this study: A generalized diagram of a nitroxyl molecule is listed as well as; VIII, 2,2,6,6-tetramethylpiperidine-1-oxyl, R = -H; I, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, R = -OH; VI, 3-carboxy-2,2,5,5-tetramethyl- pyrrolidine-1-oxyl, R = -CO$_2$H; and VII, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, R = -NH$_2$; X, Cylindrical nonpolar spin probe, amino-2,2,6,6-tetramethylpiperidine-1-oxyl 4-pyridine carboxaldimine.
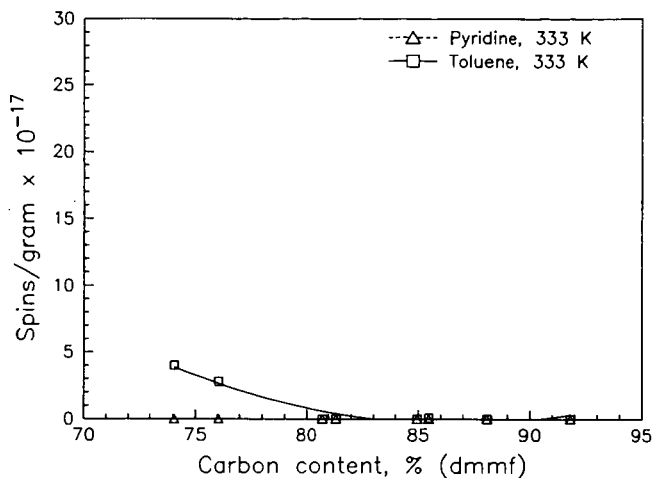
Figure 2.   Effect of solvent on the quantity of spherically shaped micropores in coal. Spin probe VIII concentration (spins/g x 10^{17} in coals swelled at 333 K in either toluene ▢ or pyridine (Δ) versus rank as % carbon on a dry, mineral matter-free (dmmf) basis.
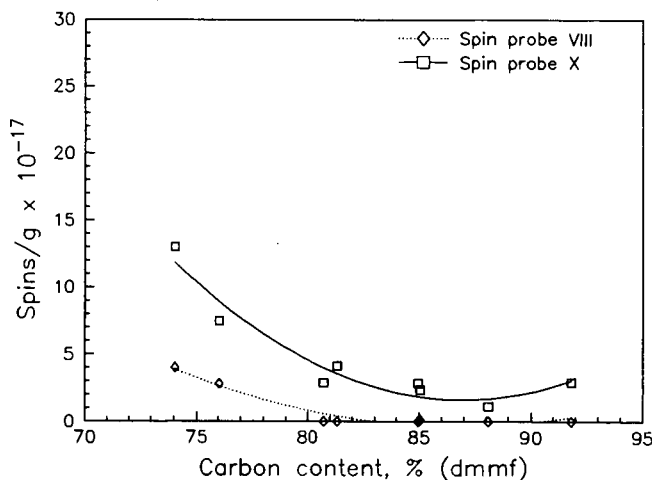

Figure 3.   Effect of solvent swelling on micropore shape/size. Spin probe X ▢ and spin probe VIII (◊) concentration (spins/g x 10^{17}) in coals swelled in toluene at 333 K, vs. carbon content (%, dmmf).
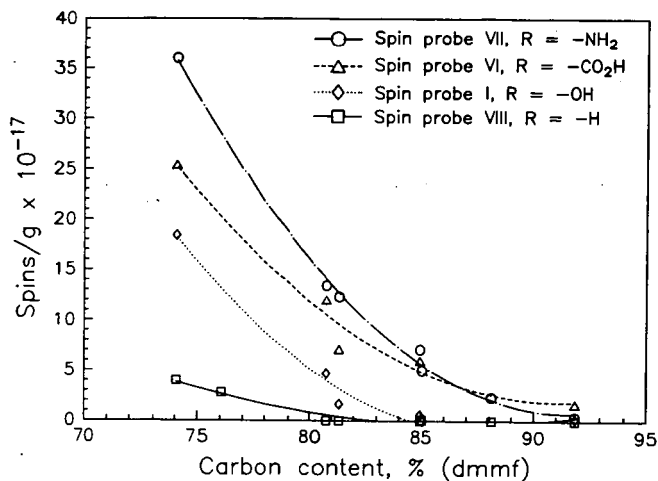
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Figure 4. Effect of spin probe R group on spin probe retention in coal for coals swelled in toluene at 333 K. Spin probe VIII, R = -H, ($\square$); spin probe I, R = -OH, ($\wedge$); spin probe VI, R = -CO_2H, ($\triangle$); and spin probe VII (O)R = -NH_2; concentration (spins/g x 10^{-17}) vs. carbon content (%, dmmf).
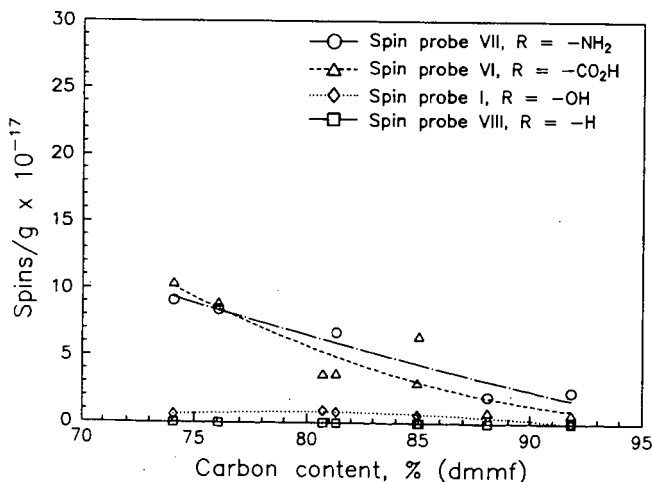

Figure 5. Effect of spin probe R group on spin probe retention in coal for coals swelled in pyridine at 333 K. Spin probe VIII, R = -H, ($\square$); spin probe I, R = -OH, ($\Diamond$); spin probe VI, R = -CO_2H, ($\triangle$); and spin probe VII(O)R = -NH_2; concentration (spins/g x 10^{-17}) vs. carbon content (%, dmmf).